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Mössbauer and T.G.A. Studies of Some Hexahalotellurate(IV) Salts

E. R. CLARK, W. R. McWHINNIE, J. MALLAKI
Department of Chemistry, University of Aston in Birmingham, Birmingham B4 7ET, U.K.

N. S. DANCE and C. H. W. JONES
Department of Chemistry, Simon Fraser University, Burnaby, B.C. V5A 1S6, Canada

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The reaction of tellurium(IV) oxide with concentrated hydrochloric acid gives a solution from which $(Ph_4As)_2TeCl_6$ *may be precipitated. This material has* ^{125}Te *Mössbauer parameters which suggest that the anion may be distorted towards* C_{3v} *symmetry. By contrast the hexabromotellurate and the hexachlorotellurate formed when a benzene solution of* $TeCl_4$ *is treated with* Ph_4AsCl *are 'normal'.*

TGA studies show that the ammonium and tetramethyl ammonium hexachloro- and hexabromotellurates decompose more or less cleanly to tellurium tetrahalide and ammonium halide. The decomposition of the tetraphenylarsonium salts is more complex.

Introduction

The demonstration, by X-ray crystallographic examination of a number of hexahalotellurate(IV) salts *e.g.* $(pyH)_2TeCl_6$ [1], K_2TeBr_6 [2], $(NH_4)_2TeBr_6$ [3], Cs_2TeBr_6 [3] and K_2TeI_6 [4], that the complex anions have regular octahedral symmetry established these materials as exceptions to the Valence Shell Electron Pair Repulsion (VSEPR) theory [5]. Das and Brown [6] recognised a low temperature tetragonal phase of $(NH_4)_2TeBr_6$ derived from the high temperature cubic phase by rotation of the anions a few degrees about the [001] direction. Although the space group (*P4/mnc*) requires $TeBr_6^{2-}$ to have not more than D_{4h} symmetry, the authors considered that the O_h symmetry was retained. Nuclear quadrupole resonance (nqr) spectroscopy can be extremely sensitive for the detection of crystallographically distinct halogens. Bull and Welsh [7] examined the nqr spectra of isomorphous trios of $TeCl_6^{2-}$, $SnCl_6^{2-}$ and $PbCl_6^{2-}$ salts in which the cation was unsymmetrical *e.g.* pyridinium. Contrary to simple expectation, the hexahalostannate(IV) salts showed the greatest sensitivity to cation effects and no evidence for measurable distortion of the hexachlorotellurate(IV) anion was found.

A recent investigation [8] of $(NMe_4)_2TeBr_6$, which is known to undergo phase transitions at lower temperatures (but which shows a single ^{79}Br nqr frequency at 80 K [9]), has indicated that the room temperature structure may not be quite that of K_2PtCl_6 and that there may be a slight flattening of the octahedron along a C_3 axis.

The stereochemical inertness of the lone pair of electrons may be explained in various ways. A molecular orbital view [10] places the $5s^2$ electron pair in an antibonding a_{1g} level. An often quoted rationalisation of the regular structure for TeX_6^{2-} (X = Cl, Br, I) is that inter ligand repulsive forces constrain the lone pair to occupy an orbital of high s character when the halogen ligand is larger than fluoride [11]. Donaldson and Silver [12] have suggested that the intense colour of salts of TeX_6^{2-} may be attributed to the population of conduction bands in the solid, thus when the $5s^2$ pair plays no steric role, electron density may be forced into conduction bands which probably involve halogen d orbitals.

We initially became interested in hexachloro- and hexabromotellurates(IV) when considering alternative synthetic routes to $TeCl_4$ and $TeBr_4$. Thus we began to investigate a range of salts by TGA. Since the cation size was varied from NH_4^+ to Ph_4As^+, we felt it would be of interest to investigate the ^{125}Te Mössbauer chemical isomer shift (δ) as a function of cation size arguing simplistically that the very large cations might increase the separation of the anions and thereby reduce the population of conduction bands. In Mössbauer terms, given that $\Delta R/R$ is positive for ^{125}Te, δ should become more positive as the cation size is increased. In the event little variation was seen but one compound $[Ph_4As]_2[TeCl_6]$ prepared from TeO_2 and concentrated hydrogen chloride provided data of interest which constitute the major justification for this paper.

TABLE I. Results of TGA Studies on Hexachloro- and Hexabromotellurate(IV) Salts. (The molecular mass of fragments lost is interpreted in terms of the most plausible molecular species).

$$[NH_4]_2[TeCl_6] \xrightarrow{215\,^\circ C-350\,^\circ C} 2[NH_4]Cl(s) + TeCl_4(g)\uparrow$$

$$[NH_4]_2[TeBr_6] \xrightarrow{240\,^\circ C-360\,^\circ C} (2-n)[NH_4]Br(s) + n[NH_4]Br(g)\uparrow + TeBr_4(g)\uparrow$$

$$[Et_4N]_2[TeCl_6] \xrightarrow{260\,^\circ C-305\,^\circ C} 2[Et_4N]Cl(s) + TeCl_4(g)\uparrow$$

$$[Et_4N]_2[TeBr_6] \xrightarrow{240\,^\circ C-340\,^\circ C} (2-n)[Et_4N]Br(s) + n[Et_4N]Br(g)\uparrow + TeBr_4(g)\uparrow$$

$$[Ph_4As]_2[TeCl_6] \xrightarrow{245\,^\circ C-335\,^\circ C} Ph_2TeCl_2(s) + Cl_2(g)\uparrow + 2Ph_3As(g)\uparrow$$

$$[Ph_4As]_2[TeBr_6] \xrightarrow{100\,^\circ C-150\,^\circ C} Ph_3As(s) + [Ph_4As][TeBr_5] + PhBr(g)\uparrow$$

TABLE II. Raman Data for Some Hexahalotellurate Salts. He–Ne Laser Excitation, $\Delta\nu$ in cm^{-1}.

	Phenyl t	$\nu_1(A_{1g})$	$\nu_2(E_g)$	$\nu_3(T_{2g})$
$[Ph_4As]_2[TeCl_6]$	240	285	270	
$[Ph_4As]_2[TeBr_6]$	238	170	150	
$[NH_4]_2[TeCl_6]$		300	250	145
$[NH_4]_2[TeBr_6]$		180	155	85
$[Et_4N]_2[TeCl_6]$		285	245	130
$[Et_4N]_2[TeBr_6]$		170	152	

Experimental and Results

Three pairs of hexahalotellurate(IV) salts were prepared: $[NH_4]_2[TeX_6]$,$[Et_4N]_2[TeX_6]$ and $[Ph_4As]_2[TeX_6]$ (X = Cl, Br). The general method of preparation was to dissolve tellurium(IV) oxide (2.0 g) in concentrated hydrochloric acid (10 ml) or hydrobromic acid (20 ml, 40%) and to treat the resulting solution with the stoicheiometric amount of the appropriate quaternary salt. $[Ph_4As]_2[TeCl_4]$ was also prepared by treating a dry benzene solution of $TeCl_4$ with the stoicheiometric quantity of $[Ph_4As]Cl$. The compounds gave satisfactory elemental analysis.

Thermogravimetric analysis of the compounds was carried out in air using a Stanton Redcroft Thermobalance (TR decimilligram model). Good reproducibility was possible for samples from different preparations of the salts using a heating rate of 10 deg. min^{-1}. Loss of particular volatile fragment often occurred over a relatively wide temperature range, and, in some cases, two processes clearly overlapped over part of the temperature range. The results are best presented in the form of annotated equations which constitute Table I. We were able to sublime $TeCl_4$ onto a cold finger by heating $[NH_4]_2[TeCl_6]$ at 260 °C under reduced pressure, thus demonstrating a convenient synthetic route from the cheaper TeO_2 to $TeCl_4$.

X-ray powder diffraction studies further confirmed the identity of the ammonium and tetraethylammonium salts. The data also excluded the inclusion of significant quantities of other tellurium compounds such as TeO_2 or $R[TeX_5]$ (which can sometimes be formed *via* a similar preparative route). The data for $[Ph_4As]_2[TeCl_6]$ prepared from TeO_2 in HCl and from $TeCl_4$ in benzene were different (Table II). The X-ray data were obtained with a Jeol JDX 7S X-ray diffractometer using Cu-K_α as a source.

Raman spectra were obtained with a Cary 81 instrument using He/Ne laser excitation. The spectra of the ammonium and tetraethylammonium salts are in excellent agreement with those published in a number of recent studies [13–16]. Unlike Adams and Morris [13] we did manage to obtain good Raman spectra of the tetraphenylarsonium salts which are of some interest. We therefore tabulate this data in Table II.

^{125}Te Mössbauer spectra were obtained as previously described [17]. In agreement with typical literature data [18, 19] no variation in δ was noted

TABLE III. ^{125}Te Mössbauer Data for Hexahalotellurate Salts Prepared in this work. (Source and Absorber at 4 K).

	δ^a (mm sec^{-1})	Δ^b (mm sec^{-1})
$[NH_4]_2[TeCl_6]$	1.73	0.0
$[Et_4N]_2[TeCl_6]$	1.74	0.0
$[Ph_4As]_2[TeCl_6]$ (from TeO_2)	1.43	0.0
$[Ph_4As]_2[TeCl_6]$ (from $TeCl_4$)	1.74	0.0
$[NH_4]_2[TeBr_6]$	1.59	0.0
$[Et_4N]_2[TeBr_6]$	1.47	0.0
$[Ph_4As]_2[TeBr_6]$	1.57	0.0

^{a}± 0.03 mm sec^{-1}, *vs.* I/Cu; ^{b}± 0.03 mm sec^{-1}.

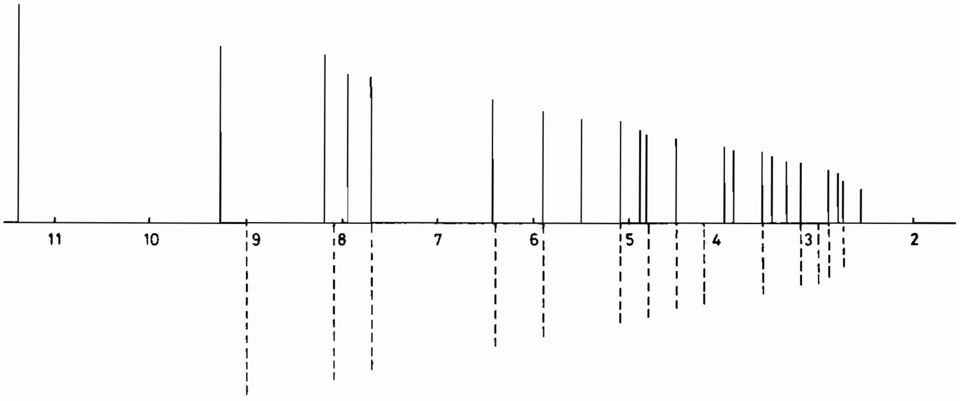

Fig. 1. 'd' Values comparison of bis(tetraphenylarsonium)hexachlorotellurate(IV). —— made from $TeCl_4$, – – – made from TeO_2.

as the cation was changed, until Ph_4As^+ was introduced. A significantly less positive chemical isomer shift was obtained when $[Ph_4As]_2[TeCl_6]$ prepared from TeO_2/HCl was investigated. However, the specimen prepared from $TeCl_4$ in benzene gave a value of δ in line with the other data. In no case was a quadrupole splitting resolvable. The data are given in Table III.

Discussion

TGA Data

The results are generally unremarkable for the ammonium and tetraethylammonium salts. Thermal decomposition of the hexachlorides is more clearly defined than for the tetrabromides and sublimation of $TeCl_4$ from $[NH_4]_2[TeCl_6]$ would appear to be a reasonable synthetic route to the tetrachloride using TeO_2 as starting material. The tetraphenylarsonium salts clearly decompose in a different manner and breakdown of Ph_4As^+ appears to occur. The reactions are, however, of no synthetic use.

Anomalous Nature of $[Ph_4As]_2[TeCl_6]$

Adams and Morris [13] obtained infra-red data for a specimen of $[Ph_4As]_2[TeCl_6]$ and observed extra bands which they considered to originate from an anion of symmetry less than O_h–C_{3v} was suggested. We have succeeded in obtaining a Raman spectrum of this compound and can confirm that the extra bands observed by Adams do indeed appear in the Raman spectrum. The Raman spectra of the other specimens are in excellent agreement with the several literature reports.

^{125}Te Mössbauer data also show $[Ph_4As]_2[TeCl_6]$ (but not the bromide) to be anomalous in the sense that a significantly less positive chemical isomer shift, compared to the ammonium and tetraethylammonium salts, is seen. We believe that this is the first time accurate data have been obtained for the tetraphenylarsonium salt although one measurement with a large experimental error is reported [20].

In the case of the hexabromotellurates and the ammonium and tetraethylammonium hexachlorotellurates, δ was insensitive to cation size thus tending to confirm trends noted in literature data. Interestingly enough, a specimen of $[Ph_4As][TeCl_6]$ prepared from the treatment of a benzene solution of tellurium tetrachloride with tetraphenylarsonium chloride, gave a Mössbauer spectrum with $\delta = 1.74$ mm sec^{-1}. X-Ray powder photographs for the two specimens were compared and significant differences noted (Fig. 1), thus it is postulated that this material may exist in at least two polymorphic forms in one of which the hexachlorotellurate anion is slightly distorted from O_h to C_{3v} symmetry. In the lower symmetry case the lone pair of electrons is probably located in an orbital of some directional character (*e.g.* directed to the centre of a triangular face of the octahedron thereby causing the distortion to C_{3v} symmetry). This would imply less s electron density at tellurium and is thus consistent with the less positive chemical isomer shift observed for the supposedly lower symmetry case. An objection to the above argument is that no quadrupole splitting is resolved for $[Ph_4As]_2[TeCl_6]$ prepared from acid media, nor is the line width abnormally large. The natural line width of the tellurium resonance line is fairly large (5.0 mm sec^{-1}) and it may be that a very small quadrupole splitting could go undetected.

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